



# Feathers, faeces and skin biopsies as non-lethal samples for mercury in marine predators from Cape Shirreff and Paradise Bay, Antarctic Peninsula.



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## Introduction

Mercury (Hg) occurs naturally in the environment, but humans have altered its natural cycling by fossil fuel combustion and mining. Mercury is a global pollution problem, due to its long distance transport and toxicity, especially methylmercury (MeHg). There are many studies examining MeHg and its trophic transfer in Northern aquatic ecosystems however much less information is available for the southern hemisphere. In Antarctica, Southern Shetland Islands and the Antarctic Peninsula are isolated coastal environments with very simple food webs.

Due to the conservation status of the Antarctic biota, feces, feathers and skin biopsies are a valid alternative to assess Hg concentrations because they: (1) are a non lethal sampling approach; (2) reflect the food source from chick(s) and mating penguins who forage in the vicinity of the breeding colonies at that time and from one individual Leopard seal; (3) reflect the difference in incorporated and excreted Hg. The influence of the diet on the observed Hg concentrations was further investigated using stable isotope ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) analysis.

## Materials and methods

### Study Area

At Cape Shirreff (62° 27' S; 60° 47' W), at the northern coast in Livingstone island, is the breeding colony of Antarctic fur seals (*Arctocephalus gazella*) most numerous of the South Shetland Islands. This place alongside Black and Williams point, plus Desolation Island, were places of hunting seals, whales and penguins, indicating high marine productivity. In its adjacent waters are records of krill and other organisms within phytoplankton and zooplankton, followed by fish, birds and marine mammals, as top predators. The chinstrap and gentoo penguins are of particular interest in this site.

Paradise bay is located in the Antarctic Peninsula (64° 49' S; 62° 51' O). One of the biggest attractions is the presence of Gentoo penguin colony with a population of approximately 3,000 individuals. Gentoo penguins nest near the base and other colonies along the coast of the island Bryde plus Antarctic shags. Small colonies of chinstrap and gentoo are located in the north coast of the island Lautaro. High marine productivity is characterized by krill. This attracts many humpback and minke whales, along with leopard seals, that feed on penguins.

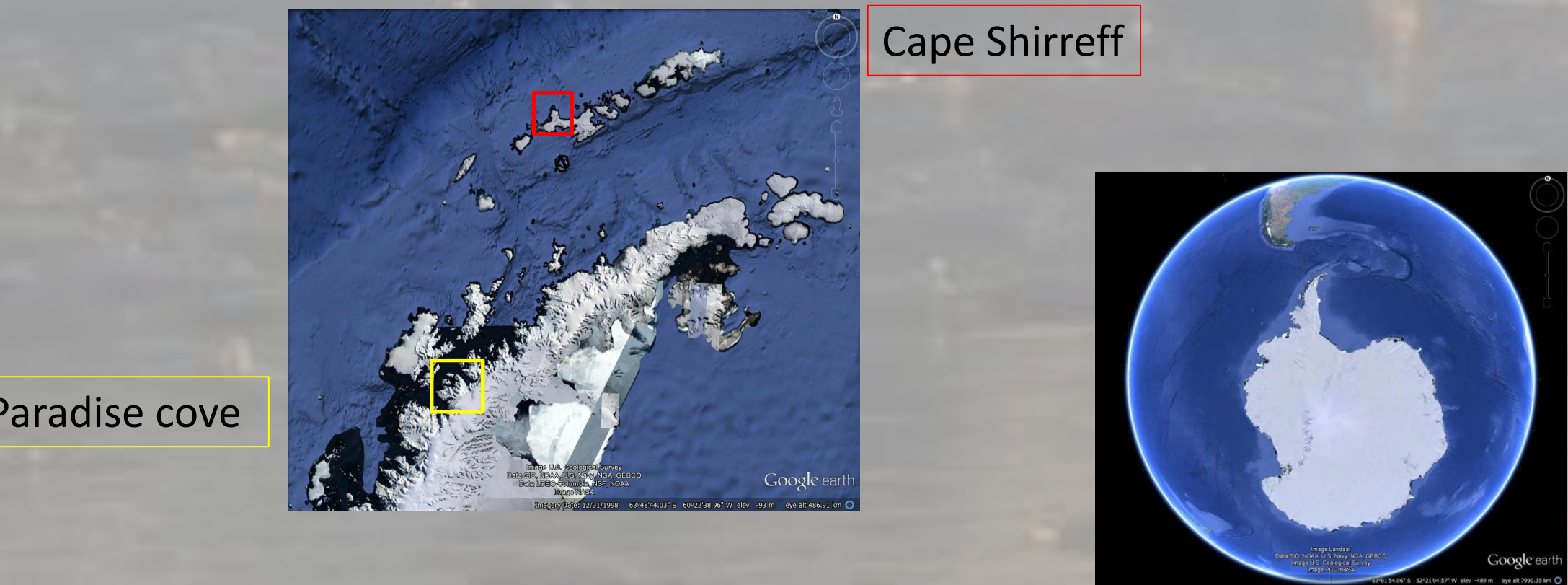
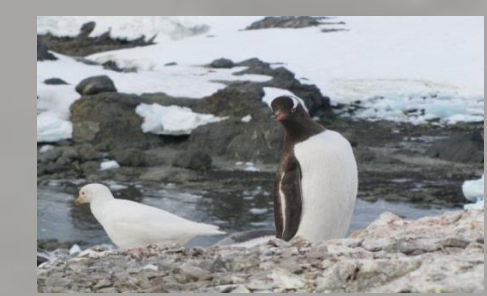
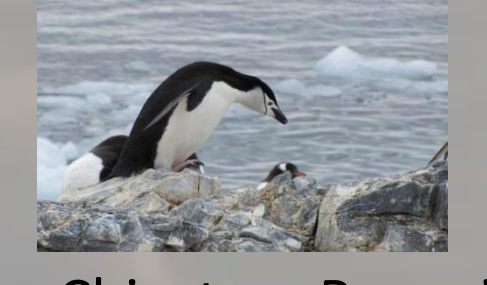


Fig 1. Sample collection sites: Cape Shirreff (Livingstone Island) and Paradise Cove (Antarctic Peninsula)



Gentoo Penguin



Chinstrap Penguin



Leopard Seal



Brown Skua

Feces stored in plastic bags at -20°C. All samples were freeze-dried prior to analysis.



Feathers from adults, stored in plastic bags at -20°C until analysis. Surface lipids and contaminants were removed using a 2:1 chloroform:methanol solution for two minutes, followed by two successive methanol rinses. Then the feathers were dried.

### Stable Isotope Analysis

Dried samples were ground and the aliquots (0.25–0.30 mg) weighed in tin cups and analysed using a Delta Plus Continuous Flow Stable Isotope Ratio Mass Spectrometer (Thermo Finnigan, Bremen, Germany) coupled to a Carlo Erba Elemental Analyzer (CHNS-O EA1108, Milan, Italy).

### Methyl Mercury Analysis

≈10 mg were analyzed by alkaline digestion, ethylation purge and trap GC-CVAFS (Gas Chromatograph–Cold Vapour Atomic Fluorescence Spectrophotometer) following U.S. EPA Method 1630 (U.S.EPA, 2001).

### Total Mercury Analysis

≈10 mg of tissue was analyzed by DMA-80.

### Quality Assurance

Certified reference materials, blanks, and replicates were analyzed within each chemical analysis.

## Results

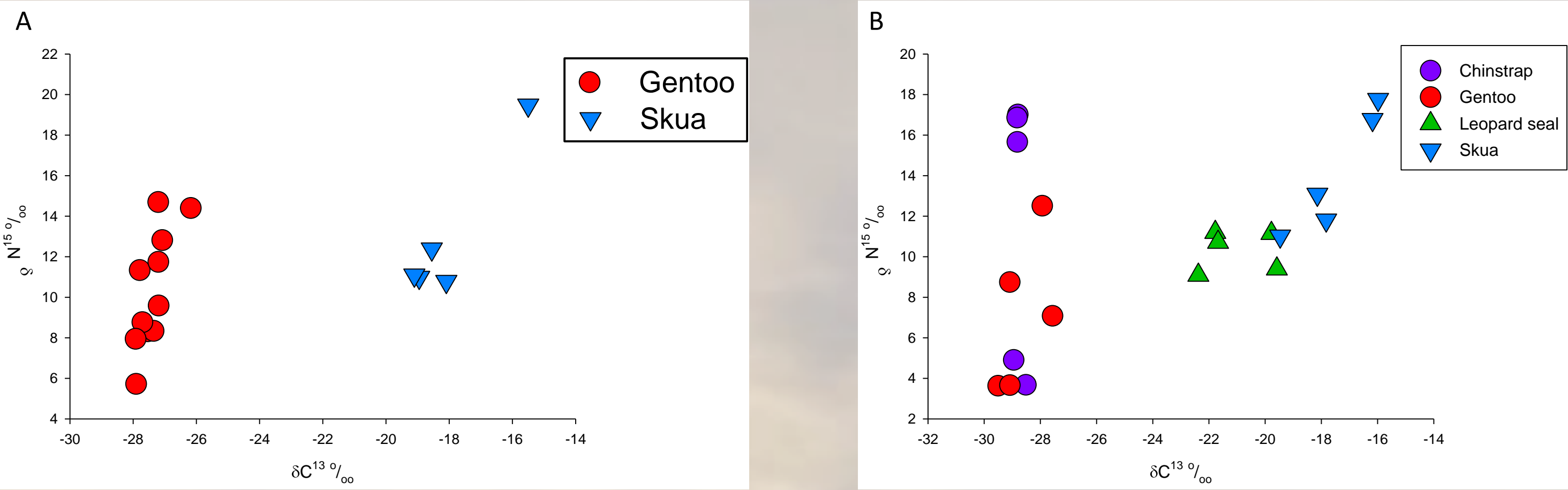


Fig 2. Stable isotope signatures ( $\delta^{15}\text{N}$  ‰ and  $\delta^{13}\text{C}$  ‰) in samples from (A) Cape Shirreff and (B) Paradise Cove areas.

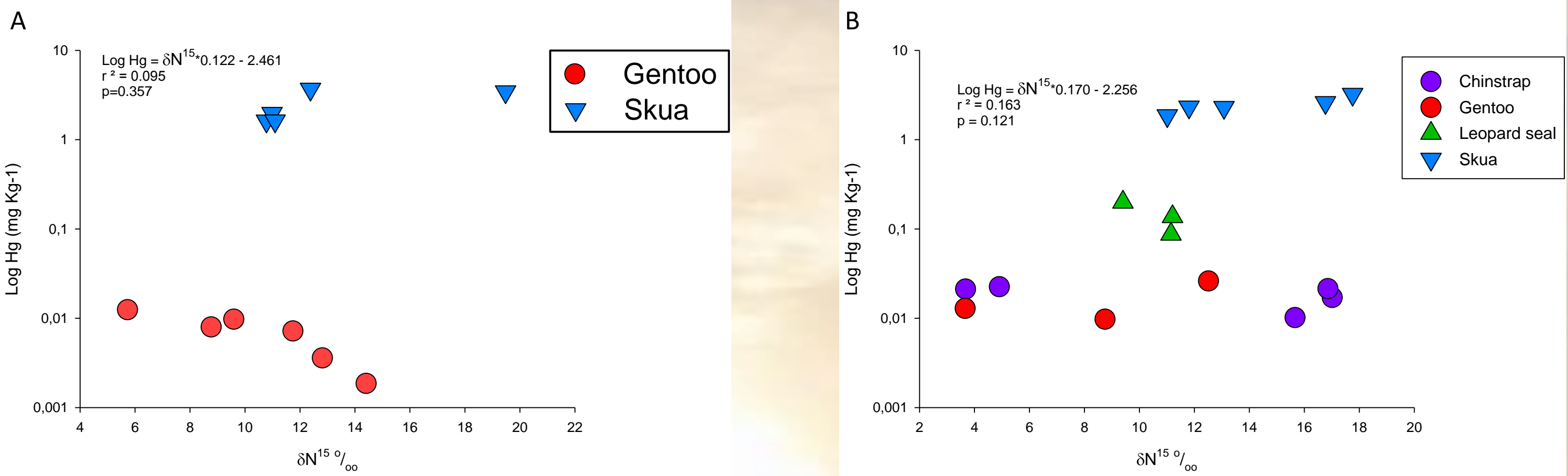


Fig 3. Mercury concentration (LogTHg for Skua and Log MeHg for penguin and leopard seal feces) and Stable isotope ( $\delta^{15}\text{N}$  ‰) regressions from Paradise Cove area (A) and Cape Shirreff (B).

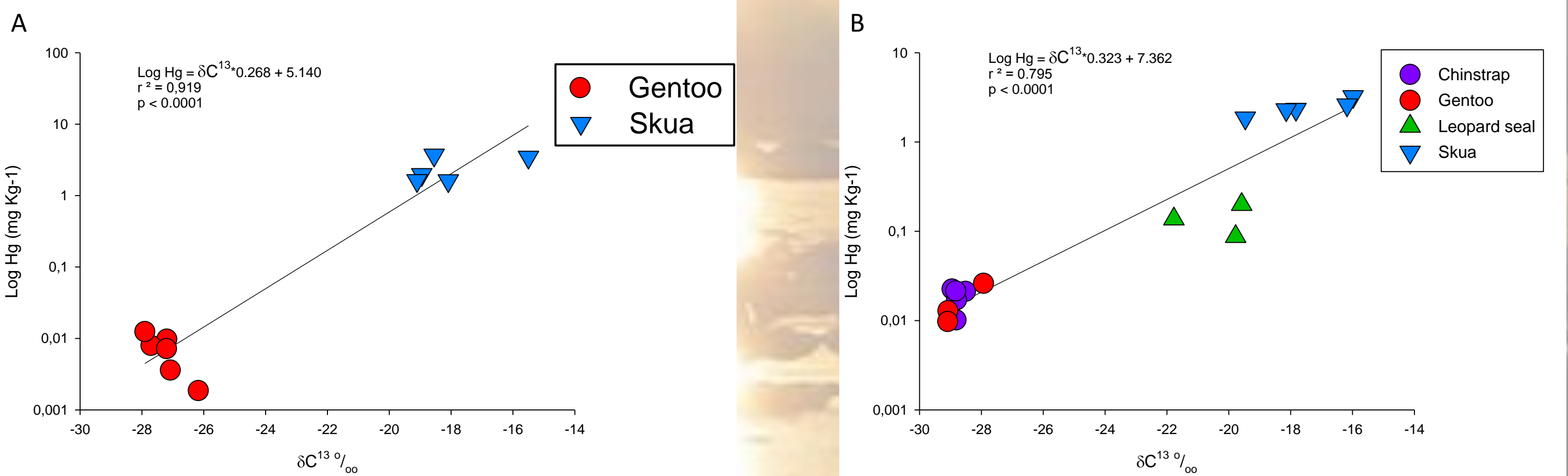


Fig 4. Mercury concentration (LogTHg for Skua and Log MeHg for penguin and leopard seal feces) and Stable isotope ( $\delta^{13}\text{C}$  ‰) regressions from Paradise Cove area (A) and Cape Shirreff (B).



Leopard seals



Gentoo penguins



Chinstrap penguins



Skuas

• The isotopic signal in the feces showed that penguin species are feeding on a wide range of trophic levels ( $\delta^{15}\text{N}$ ), within the same foraging habitat (very narrow  $\delta^{13}\text{C}$  signature) on both sites (Figs 1, A&B).

• Skuas showed a wider range of food source (Fig 2 A & B) (higher variability in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ), while leopard seals isotopic values showed a more specific prey source (Fig 2 B). Leopard seal feces and skua feathers isotopic values showed a possible overlapping in diet.

• Analysis showed large differences in Hg concentrations that are related to trophic position ( $\delta^{15}\text{N}$ , Figs 3 A&B), but specially to foraging habitat ( $\delta^{13}\text{C}$ , Figs 4 A&B).

• MeHg excretion was very low and variable between species (Figs 5-6). MeHg excretion by Penguins was ≈12 fold lower than Total Hg. Less than 34% of TotHg was MeHg in feces → Chinstrap penguins (16.3-33.3%), Gentoo penguins (4.2-20.5%), Leopard seals (4.1-15.6%).

## Discussion & Conclusions

• Mercury concentrations and stable isotopes in feces and feathers showed that differences could be attributed to trophic level and carbon source. Differences in the diet of these species has been previously reported. Chinstrap penguin feed primarily on krill, although they may have a broader diet that includes fish and zooplankton. Gentoo penguins prey on higher trophic levels. Skuas prey primary on penguin chicks, but can also act as scavengers, stealing food from Leopard seals (fur seal cubs). Higher levels of Hg related to carbon source could be explained by inshore foraging, which is in agreement with the MeHg enrichment of coastal benthic areas (Fitzgerald et al., 2007).

• As feces are the product of feeding habits of penguins and seals, these samples are explaining

mercury concentration in the aquatic food web of both sites, more than the intake by penguins and seals.

• The differences in trophic position and diet shows that using feces as a proxy is critical to identify possible dietary sources of mercury and its biomagnification in Antarctica. Despite this fact, samples of penguins feathers and seal tissue are under analysis to assess the Hg intake.

• MeHg results are consistent with data from other cold environments. MeHg excretion was lower > 12 fold than Total Hg. MeHg elimination has been inversely correlated to water temperature (Trudel & Rasmussen, 1997), which suggesting that in Antarctic waters its excretion is inhibited, and explaining the low concentrations of MeHg in feces and the very high concentration in feathers (Bond and Diamond 2009, Thompson and Furnasse, 1989).

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